



PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of:

) Paper No. 7

APPLICANTS: GEORGE E. MORRIS,  
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04249

PATENT TRADEMARK OFFICE

SERIAL NO: 09/779287

) Group Art Unit:

FILED: February 8, 2001

) Examiner:

WALTER DEAN  
GRIFFIN

FOR: PREPARATION OF COMPONENTS  
FOR TRANSPORTATION FUELS

) Attorney Docket  
) No.: 37,248.04

**DECLARATION UNDER 37 CFR § 1.131**

Assistant Commissioner for Patents  
Washington, DC 20231

ANY ADDITIONAL FEES REQUIRED  
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on February 5 2003. By Carol M. Neth  
(Date) (Signature)

CAROL M. NETH  
(Typed or Printed Name of Person Signing Certificate)

Examiner Griffin:

George Ernest Morris, Andrew Richard Lucy, William H. Gong,  
5 Monica C. Regalbuto and George A. Huff, Jr. hereby solemnly  
declare that:

1. They are the inventors who, on February 8, 2001, filed  
the above-identified application Serial No. 09/779,287.

2. They completed the invention, which is set forth in the  
10 above-identified application Serial No. 09/779,287, in the United  
States of America and the United Kingdom prior to September 28,  
2000, the filing date of the application from which U.S. Patent No.  
6,402,939 (Yen et al.) matured.

3. Prior to September 28, 2000, their invention as  
15 described and claimed in the subject application was completed in  
the United Kingdom, as evidenced by Laboratory Notebook 1396,  
pages 1 to 6, identified as EXHIBIT A, which illustrates the key  
points of declarants' process for oxidative desulfurization of a high  
boiling cut of a hydrotreated diesel material. These pages  
20 memorialize and record experiments carried out in Hull, United  
Kingdom, a WTO member country, which serve to complete  
reduction to practice of the aforesaid invention.

4. To provide the higher boiling feedstock for the work at  
Hull, a hydrotreated refinery distillate was partitioned by distillation  
25 experiments carried out in United States under the supervision of  
Monica C. Regalbuto who is one of the undersigned declarants.

5. Under the supervision of Dr. George E. Morris, who is one of  
the undersigned declarants, Mr. Peter Anderson and Mr. Andrew  
Blanchard, Research Technicians, Hull Research Center, Hull, UK,  
30 conducted oxidation-simultaneous extraction experiments described in

a BP Chemicals Limited Laboratory Note Book 1396, pages 2 to 6. The work described shows that the sulfur species concentrated in a higher boiling cut of a hydrosulfurized diesel material was oxidized with a soluble quaternary ammonium salt in an immiscible aqueous phase comprising hydrogen peroxide and phosphotungstic acid; separation from the reaction mixture of both an organic liquid and immiscible aqueous phase containing a portion of the oxidized sulfur species; and further removal of the oxidized sulfur species by silica sorption. The aqueous hydrogen peroxide phase and catalyst system can be reused with a fresh diesel charge. Comparative examples (not described in pages of the exhibit) showed that for the same reaction times and overall hydrogen peroxide usage greater amount of sulfur are treated and removed from the higher boiling cut than the corresponding full range material.

6. In this work Mr. Anderson charged a suitably equipped nitrogen purged glass reactor with S-25-288C-FBP (251.2 g), a.k.a. LS-98-25 (550°F FBP), aqueous hydrogen peroxide (61.6 g of 26.0 percent by weight), Aliquat® 336 (1.45 g) and an aqueous solution of phosphotungstic acid (0.83 g in 5.6 g water) and water (126.0 g). The hydrogen peroxide was equivalent to 8.2 percent by weight in the total aqueous phase. The reaction mixture was heated to 60° C. with stirring during 30 minutes and maintained at 60° C. with stirring during 4 hours. After cooling to ambient temperature the organic phase (248.9 g) was separated from the aqueous phase (189.3 g) and another, viscous brown oily phase. A sample of the organic phase was identified as PS-25-288C-FBP and retained for analysis which gave 43 ppm sulfur and 29 ppm nitrogen. The recovered aqueous phase contained 6.9 percent by weight hydrogen peroxide. The viscous brown oily phase was dissolved in methanol (40.0 g, recovered 42.0 g). Analysis of the methanol solution gave 30 ppm sulfur and 1100 ppm nitrogen.

7. Similar portions of PS-25-288C-FBP (total 186.1 g) were passed through one of two silica columns (11.9 g each). Analysis of

the product recovered (156.2 g) after silica treatment gave 0.3 ppm sulfur and 2.5 ppm nitrogen. A band of dark brown material was retained on the silica. The brown band was eluted from the column with methanol (23.0 g). On analysis it was found to contain 110 ppm sulfur and 58 ppm nitrogen.

8. Copies of the above referenced Laboratory Notebook pages are attached as Exhibits. The Exhibits are a true copy, except that the dates thereof and unrelated subject matter have been blanked-out, but all the dates are prior to September 28, 2000.

9. The undersigned declare further that all statements made herein of their own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

G E M

GEORGE ERNEST MORRIS

Date 28 JANUARY 2003

A. Lucy

ANDREW RICHARD LUCY

Date 28<sup>th</sup> JANUARY 2003.

William H. Gong

WILLIAM H. GONG

Date Feb. 3, 2003

Monica C. Regalbuto

MONICA CRISTINA REGALBUTO

Date Jan. 30, 2003

George A. Huff Jr.

GEORGE A. HUFF JR.

Date Feb 3, 2003

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Serial No. 09/779,287

Declaration under Rule 1.131

EXHIBIT A



**BP CHEMICALS LIMITED**

**HULL RESEARCH CENTRE**

**LABORATORY  
NOTE BOOK**

1396

OXIDATIVE DESULFURIZATION  
OF DIESEL FUEL.

2

This work is a continuation of a series of experiments investigating reduction of sulphur concentration in diesel fuel using an oxidative process. Initial experiments are recorded in Laboratory note book 1292 pages 103 - 152.

Oxidative desulphurization of diesel sample LS-98-25/ 550°F F.B.P.  
4 hour reaction duration

Date:

Ref: 1396/002

Aim This reaction is the first in a series of experiments in which we will evaluate the time dependency of the rate of oxidative desulphurization in a sample of diesel oil with fractional boiling point split  $> 550^{\circ}\text{F}$  containing approx. 60 ppm sulphur. Data collected from this and other reactions in the series will be used to construct a mass balance showing the distribution of phase transfer agent, catalyst and sulphur.

Reaction charge

	<u>Required (g)</u>	<u>Actual (g)</u>
Oil phase LS-98-25 (550°F F.B.P.)	250.00	251.71
Aliquat 336®	1.45	1.45
Water	125.14	125.96
26% Hydrogen peroxide Sol <sup>n</sup>	61.60	61.58
Phosphotungstic acid	0.81	0.827
in water	4.86	5.575

Cont.

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3

All the listed material were charged directly into a 2 ltr. reaction flask fitted with stirrer ( $\sim 300$  r.p.m) and overhead water cooled condenser. The contents of the reactor were heated to  $60^{\circ}\text{C}$  and held at that temperature for four hours.

### Record of reaction temperature.

Time (H.m.)	Elapsed time (m)	Temperature ( $^{\circ}\text{C}$ )	
		Contents	Shaker
09:30	-	23	-
10:00	0	59	$< 140^{\circ}\text{C}$
10:30	30	63	$< 140^{\circ}\text{C}$
11:00	60	60	$< 110^{\circ}\text{C}$
11:30	90	60	As above, "
12:00	120	60	-
12:30	150	60	-
13:00	180	60	-
13:30	210	60	-
14:00	240	60	-

Reaction was shut down at 14:00m heater lowered and allowed to cool below  $25^{\circ}\text{C}$  before transfer to separation funnel.

Total mass of reaction product = 440.14g

### Liquid / Liquid Separation

Mass of separated Aqueous phase = 189.27g

\* Mass of heavy brown phase = 2.00g

Mass of diesel phase = 248.87g

\* The heavy brown material was collected from the reaction flask and the separation funnel by first charging 40.0g methanol into the reaction flask shaking to dissolve, then transferring into the separation funnel shaking to dissolve. A mass increase of 2g was observed by solution wt. = 42.0g.



Loading Silica absorption column,

C3

C1

C2

183.30

loaded with silica

163.34

162.21

172.50 g

Un loaded column mass

151.47 g

150.28

10.80 g

Mass of silica

11.87

11.93

Not used, Col + Retained oil + Silica (g)

178.06

175.50

Retained oil

14.72

13.29

62.77g Sample of whole oxidative oil phase taken  
for Ref. and analysis. Mass of diesel passed over  
silica columns =  $248.87g - 62.77 = 186.10g$

1<sup>st</sup> column Mass of 1<sup>st</sup> fraction collected from base of silica column = 93.24

2<sup>nd</sup> column Mass of 2<sup>nd</sup> fraction collected from base of silica column = 62.92g  
Total = 156.16

Retained mass of oil  
on columns = 28.01

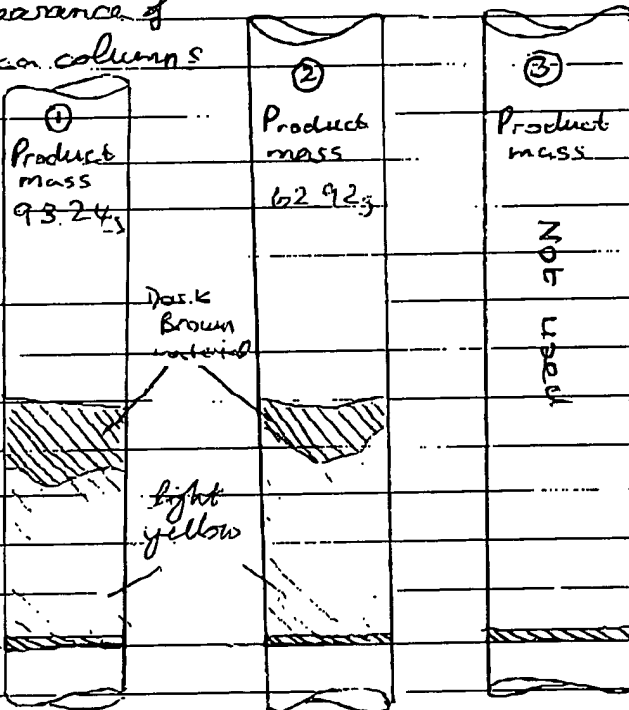
Appearance of  
Silica columns

Notes:

① Because of the apparent higher  
concentration of heavy brown material  
in the whole oxidative oil product  
the rate was greatly reduced.

This reduction in flow rate was  
a result of a dense band of brown  
material which formed within the  
top 1cm of the silica column.

② Because of the low flow rate  
two additional silica adsorption  
columns were set-up to process  
the remaining oil phase.  
Column 3 not used.



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5

Analysis of aqueous phase for hydrogen peroxideDilution of aqueous phase

Mass of aqueous phase = 4.60 g  
 added water = 48.07 g

Dilution factor =  $52.67 / 4.60 = 11.45$

Analysis

	A	B	C
Sample wt. (g)	2.24	2.31	2.56
Final titre vol. (cm <sup>3</sup> )	41.00	49.60	47.20
Init. titre vol. (cm <sup>3</sup> )	32.90	41.15	38.50
titre vol (cm <sup>3</sup> )	8.10	8.45	8.70

Calculations

$$A \quad \frac{8.1 \times 0.1 \times 1.701}{2.24} \times 11.45 = 7.04 \% \text{ wt.}$$

$$B \quad \frac{8.45 \times 0.1 \times 1.701}{2.31} \times 11.45 = 7.12 \% \text{ wt.}$$

$$C \quad \frac{8.70 \times 0.1 \times 1.701}{2.56} \times 11.45 = 6.62 \% \text{ wt.}$$

Mean value 6.93 %wt. hydrogen peroxide

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Methanol washing of to 2 cm of silica adsorption columns.

Both of the silica adsorption columns were washed with  
~ 20g methanol to produce a solution of the brown material  
retained on the top two cm. of each column.

This solution would be assessed for solid content and  
sent for Nitrogen, Sulphur and Tungsten analysis.

Assessment of % solid in solutions of heavy brown oil and estimation  
of the actual mass of this material produced during the reactions.

#### Solid content of heavy brown substance in methanol solution

Residual material washed from base of reaction flask and separating funnel

	1	2	3
Dish plus dried solid	1.9568	1.9242	2.0129
Dish plus solution	2.5583	2.5332	2.7312
Empty dish	1.9208	1.8871	1.9694
Wt. of solution	0.6375	0.6661	0.7618
Wt. of solid	0.036	0.0371	0.0435
% solid in solution	5.647059	5.569734	5.71016

Mean Value 5.642318

Mass of methanol post washing (g) 42  
 Mass of brown heavy oil (g) 2.269779

Solution obtained from washing the top two cm of the silica column with methanol

	1	2	3
Dish plus dried solid	2.6234	2.5924	2.328
Dish plus solution	3.4791	3.248	2.9724
Empty dish	2.8064	2.578	2.222
Wt. of solution	0.6727	0.673	0.6504
Wt. of solid	0.017	0.0174	0.016
% solid in solution	2.527129	2.585438	2.460025

Mean Value 2.524197

Mass of methanol post washing (g) 23  
 Mass of brown heavy oil (g) 0.580565

Total mass of brown material (g) 2.950339

Note: In the first reaction of this series which evaluated the oxidative  
desulphurisation of the full sample the mass of brown material  
produced was estimated to be 2.1g ~  $\frac{1}{3}$  lower than that  
produced in this experiment conducted with the  
higher boiling point material.

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